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Bradley Shogrin
Case Western Reserve University
Cleveland, Ohio

William R. Jones, Jr.
Lewis Research Center
Cleveland, Ohio

and

Pilar Herrera-Fierro
Ohio Aerospace Institute
Cleveland, Ohio

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DEWETTING OF A PERFLUOROPOLYETHER
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Bradley Shogrin
Case Western Reserve University
Cleveland, Ohio 44106

William R. Jones, Jr.
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

and

Pilar Herrera-Fierro
Ohio Aerospace Institute
Cleveland, Ohio 44142

ABSTRACT

Eight different production lots of a commercial perfluoropolyether (PFPE) based on hexafluoropropene oxide (HFPO) were applied to polished metal surfaces by spinning. One of the lots repeatedly dewetted from a clean 440C steel surface, forming droplets on the surface, whereas the other seven did not dewet. This dewetting phenomenon also repeatedly occurred on 2024 aluminum and 1018 steel, but not on copper or gold. Fourier Transform Infrared Microspectroscopy (μ -FTIR) was used to determine thickness and uniformity of the PFPE films. The dewetting lot was found to dewet from 440C steel at a film thickness greater than 520 Å. A portion of the dewetting lot was heated at 316 °C for 12 days in the presence of oxygen and M-50 steel. This fluid did not dewet. Sequentially, samples of the dewetting lot were filtered either with an alumina or a silica cartridge which can remove polar impurities. Neither of the filtered samples dewetted from 440C steel. It was concluded that an unknown impurity, both thermally labile and polar, present at very low concentration and undetected by our analytical techniques (FTIR, proton NMR, or F^{19} NMR), was responsible for the dewetting phenomenon.

INTRODUCTION

Perfluoropolyethers (PFPE) are a class of liquid lubricants which have been used for many space applications for over 30 years (1), (2). In addition, these fluids are considered to be excellent candidates for advanced high temperature aeronautical applications (3), (4). One member of this class based on poly (hexafluoropropene oxide) (HFPO) has been commercially available since the 1960's (5).

Many different properties of poly (HFPO) have been studied. These include: thermal stability (6), oxidative stability (7), stability in the presence of Lewis acids (8)-(10), elastohydrodynamic behavior (11), pressure-viscosity characteristics (12), electron beam (13) and X-Ray damage (14), surface migration (15), conformation (16) and tribochemical degradation (17), (18).

Poly (HFPO) fluids are known to contain thermally labile impurities which can adversely affect thermal and oxidative stability (6), (7). These impurities may be hydrogen end-capped chains, peroxides, carbonyl groups, or other functional groups not represented by the normal HFPO structure. Thermal pretreatments in the presence of oxygen and a catalyst have been used in the past to remove these impurities and, thus, improve thermal stability (7). Of these impurities, hydrogen end-capped chains ($-OCHF_2CF_3$) are the most prevalent (7), (19).

Recently, a portion of a particular lot (29-2) of a poly (HFPO) fluid (143AC) was thermally treated to remove labile impurities (19). This was accomplished by heating in oxygen at 343 °C for varying periods of time. The hydrogen end-

capped chains, which are easily detected by various techniques, such as Fourier transform infrared spectroscopy (20), were effectively removed. Surprisingly, this thermal treatment, which had been successful in the past in stabilizing poly (HFPO) fluids (7), failed to render it completely stable in oxidizing atmospheres at 316 °C in the presence of metal alloys (19). It was concluded that a functional group, not represented by the normal HFPO structure, was responsible for this residual instability.

In a parallel study thin films of this fluid lot (not thermally treated) were deposited onto 440C steel specimens for a series of tribotests. During deposition an unusual dewetting phenomena occurred. The objective of this paper is to describe the phenomenon, attempt to characterize it, and discuss its tribological implications.

EXPERIMENTAL

Fluids

Several lots of a commercially available poly (hexafluoropropene) fluid were studied. The fluid that exhibited the unusual behavior will be referred to as AC (29-2). Two other commercial PFPE fluids and a perfluoro acid were used to simulate possible contaminants. One PFPE fluid was a poly (HFPO) hydrogen end-capped fluid (E-11) where each chain is terminated with (-OCHF₂CF₃). The other PFPE fluid was a poly (HFPO) fluid (157 FSM) where each chain is terminated with (-COOH). The acid used as a simulative contaminant was perfluorooctanoic acid. In an effort to try to eliminate thermally labile impurities that may have been present in AC (29-2), a portion of this lot was thermally treated in oxygen at 316 °C for 12 days in the presence of M-50 steel. The thermal treatment apparatus and procedure are fully described in reference 19.

Specimens and Surface Preparation

Test specimens consisted of discs (17.5 mm in diameter and 4.76 mm in thickness) made of 440C stainless steel, 2024 aluminum, 1018 steel, copper and steel coated with gold. The specimens were polished on microcloths with 0.3 μm alumina and tap water. Polishing was repeated twice, using a clean microcloth, and resulted in an arithmetic roughness average (R_a) of ≈0.01 μm measured with a commercial surface profilometer. Specimens were rinsed with tap water after polishing to remove any residual alumina. After the final polishing step, specimens were dried, and ultrasonically cleaned in hexane, followed by acetone, and finally methanol for approximately ten minutes each. Specimens were then blown dry with nitrogen and promptly covered to minimize dust contamination. Following this, the specimens were UV/ozone treated for 15 minutes in a commercial apparatus (21) to remove carbonaceous contamination. Application of the PFPE films followed within 5 minutes of the UV/ozone cleaning.

Application of Lubricant Films by Spinning

A few drops of the neat PFPE were placed on the specimen using a disposable glass pipette, while tilting and rotating the specimen, so that the entire surface was wetted by the gravity driven drops. The specimen was then axially centered on the driving shaft of a centrifuge, covered and allowed to stand for several minutes. The specimen was then spun at 5000 rpm (maximum radial acceleration of 250g) for 30 minutes.

Application of Lubricant Films by Deposition from Solution

Thin film deposition was accomplished by using the apparatus shown in Fig. 1. This is a derivative of the deposition process known as dip-coating. In this process (22) a specimen is coated by slowly withdrawing it at a constant speed from a solution of the lubricant in a volatile solvent. As the solvent evaporates, a thin film of the nonvolatile lubricant remains on the

surface. In this procedure, both solution concentration and withdrawal speed, are important parameters. For the apparatus used in this study, gravity driven solution flows past the stationary specimen. Several concentrations of poly (HFPO) fluids (2 to 4 grams in 100 ml of solvent) were used. The solvent used was a perfluorinated cyclobutane. The recession rate of the fluid on the surface was approximately 0.8 mm/sec.

Lubricant Film Thickness Measurements

The thickness of the poly (HFPO) fluids on each specimen, either from spinning or from the deposition apparatus, was measured using an infrared microscope (μ -FTIR) in the reflectance mode using a Grazing Angle Objective (GAO). A gold coated glass slide was used to acquire the background spectrum. Absorbance as a function of wave number was determined for each film at three different radii on the specimens' surface, approximately 120° apart using an analysis spot diameter of 100 μ m.

The films measured absorbance is then compared to the thickness-dependent absorbance calculated from thin film Fresnel reflectance theory (23) using known HFPO optical constants (16). The theoretical results were independently checked by variable angle spectroscopic ellipsometry (VASE) measurements on actual HFPO films and found to agree within $\pm 15\%$. The results of this work, plotted as absorbance of the 1313 cm^{-1} absorption band as a function of film thickness, are shown in Fig. 2. After experimentally obtaining the absorbance of the 1313 cm^{-1} band on the coated discs, the corresponding film thickness was obtained using Fig. 2.

Spinning yielded a uniform film thickness of $1750 \text{ \AA} \pm 15\%$ on 440C steel. The deposition apparatus produced thinner film thicknesses ranging, from 210 to 560 Å . Film thickness as a function of solution concentration appears in Fig. 3. The hollow squares represent the full range of observed experimental values, whereas the solid circles signify the average of the experimental values. Lubricant uniformity across any one surface was $\pm 15\%$. The error associated with surface-to-surface film thickness repeatability was $\pm 20\%$.

RESULTS

Films Applied by Spinning

Immediately after being spun, lot AC (29-2) began to dewet from 440C steel, 2024 aluminum, and 1018 steel, forming droplets on these surfaces. Dewetting of this lot was repeatedly seen on these surfaces, but not from copper or gold. Seven different commercial lots were applied in a similar fashion and did not dewet from 440C steel. The thermally stressed lot AC (29-2) did not dewet from 440C steel. Figures 4(a) to (d) contains micrographs of deposited films on 440C steel for poly (HFPO) AC lots (29-2), MLO 71-6, 124, and 150, respectively. Figure 4(a) shows the dewetting phenomena clearly, as the film has retracted into droplets, ranging in diameter from 10 to 200 μ m. Figures 4(b) to (d) show non dewetting behavior. There is some nonuniformity of the films due to surface defects. Figures 5(a) to (d) show the behavior of lot AC (29-2) on surfaces of 2024 aluminum, 1018 steel, copper and gold respectively. Again, spontaneous dewetting occurred on the aluminum and 1018 steel, but not on copper or gold.

Films Applied with the Film Deposition Device

A series of different film thicknesses of AC (29-2) were deposited on 440C. Film thicknesses $\leq 350 \text{ Å}$ did not dewet. However, film thicknesses $\geq 520 \text{ Å}$ dewetted from the 440C surface.

Previous Chemical Analysis

In previous work (19), lot AC (29-2) was analyzed by transmission IR, proton NMR and F^{19} NMR. The usual hydrogen end-capped impurity ($-OCHF_2CF_3$) and a structural arrangement $[-OCF_2CF(CF_2OR_f)OCF(CF_3)CF_2-]$ not represented by the basic poly (HFPO) formula, were found. However, there were no impurities of a polar nature detected. Thermal oxidative treatment did effectively remove the hydrogen impurity to below detectable limits (< 1 ppm), but had no effect on the second impurity.

Contaminated Film Application

Since the thermal treatment removed the hydrogen impurity and the resulting fluid did not dewet, it was originally implicated as the possible source. A second possible impurity, which would also be removed by thermal treatment, is carboxylic acid terminated chains. Therefore, in order to simulate these impurities, 0.1 gram of HFPO fluid 157 FSM (long HFPO polymer chains terminated with $-COOH$) was mixed with 0.2 ml of the previously non-dewetting lot 147 and applied to multiple 440C surfaces by spinning. Afterwards, 0.1 ml of the HFPO fluid E-11 (hydrogen end capped polymer chains) was added to the above mixture and applied to multiple 440C surfaces by spinning. None of the surfaces that had either of these two mixtures applied to them dewetted.

Another simulative impurity, a short chain perfluorinated acid (perfluorooctanoic acid), was dissolved into non-dewetting lot 2 at various concentrations ranging from <0.0003 to 0.3820 wt %. The solutions were then heated to $50^\circ C$ for 12 hours. Each solution was applied to 440C steel and subsequently dewetted from it. The dewetting behavior of the lowest acid concentration was similar to that of AC (29-2). The dewetting behavior became more severe, as both the rate of retraction of the solution into droplets and the minimum film thickness before the onset of dewetting increased with increasing acid concentration. To determine if the acid was detectable in these solutions, each was analyzed with the FTIR in transmission mode using a 1 mm fixed-path-length liquid cell. The absorbance of the perfluorinated acid's carbonyl peak (1775 cm^{-1}) was measured, and the data fitted using Beer's Law for Solutions. The resulting plot is shown in Fig. 6. Neither of the two solutions of lowest acid concentration (<0.0003 and 0.0108 wt %) had detectable carbonyl peaks. The FTIR detectability limit of the acid's carbonyl peak was taken as the zero intercept of the absorbance axis and was found to be 0.0115 wt % acid in solution.

Filtered Film Application

The dewetting lot was repeatedly applied to 440C surfaces by spinning after being filtered through either an alumina or a silica cartridge. The cartridges are designed to filter out polar components. Dewetting was not observed after AC (29-2) had been filtered by either cartridge.

DISCUSSION

When a liquid contacts a solid non-porous solid surface, two things may occur. The liquid may spread completely to wet the surface (forming a film of zero contact angle) or it may partially wet the surface (forming a film of finite contact angle). If the liquid is an organic material such as a lubricant, its surface tension (energy) is typically, $< 100\text{ ergs/cm}^2$ at room temperature. Metals have surface energies ranging from 500 to 5000 ergs/cm^2 . One would then expect a lubricant to spread readily on any clean, high energy surface, thereby decreasing the free energy of the system (24).

However, there are examples of pure organic fluids that do yield non-wetting behavior on high energy surfaces. Hare and Zisman (25) described this behavior and termed these fluids as "autophobic." Examples of autophobic fluids are: 1-octanol, trichlorodiphenyl and tri-*o*-cresyl phosphate. It was theorized that when an autophobic fluid contacts the metal surface, fluid molecules adsorb at the fluid/solid interface. This adsorbed film forms a surface having a surface energy less than the surface

tension (energy) of the bulk fluid. Thus, after the fluid apparently wets the surface, it retracts forming droplets having finite contact angles. Some synthetic liquid lubricants, such as polyphenyl ethers, behave in this manner (26). This is an inherent property of autophobic fluids and is not associated with an impurity.

A similar phenomenon can occur if a surface active impurity is present which can adsorb at the fluid/solid interface forming a low energy surface. The overlying fluid, now in contact with a low energy surface, will retract into droplets. The dewetting PFPE lot was analyzed earlier (19) by FTIR, proton and ^{19}F NMR. As mentioned above, no polar impurities were detected. Some hydrogen terminated chains and a structural moiety not represented by the normal HFPO structure were found. It is well known that poly (HFPO) fluid degradation can produce acid fluorides (8), (9). Acid fluorides hydrolyze to acids in the presence of moisture. It is also known that perfluorinated acids, such as neat (100 percent) perfluorodecanoic acid exhibit autophobic behavior (27). Of course, one would not expect the presence of these materials in an unused fluid.

Nevertheless, it is obvious that a polar impurity is present in lot AC (29-2). This impurity is present at a low enough concentration as to escape detection by our chemical analytical techniques. On selected clean, high energy surfaces (440C and 1018 steels, and 2024 Al), it is assumed that it segregates to the metal/fluid interface yielding a low energy surface that causes a retraction of the overlying fluid. Apparently, the impurity does not form a coherent surface film on less chemically active surfaces, such as gold and copper.

Although not identified, one can speculate that the impurity is probably a short chain carboxylic acid generated by chain scission during production and not totally removed during final processing. A short chain acid is more likely than a longer chain because of the ease of forming a coherent adlinear adsorbed surface film. The long HFPO chain on the carboxylic acid terminated PFPE (157 FSM) would not lend itself to form a compact surface film. And in fact, this simulated impurity did not produce a dewetting situation when used as an additive, or as the neat fluid.

Tribological Implications

For a lubricated contact, the supply of lubricant must be maintained throughout the life of the mechanism. If this supply is disrupted or reduced, the life of the mechanism may be drastically reduced. The operational life of a ball bearing contact, as illustrated in Fig. 7, is intimately related to the ability of an elastohydrodynamic (EHL) film to separate the bearing surfaces sufficiently so that asperity contact can be reduced or eliminated (28). A fundamental feature of EHL is that film thickness is determined by the EHL pressure generated in the convergent inlet region. If there is an insufficient supply of lubricant in the inlet region, this EHL pressure generation will be inhibited and the resulting film thickness will be diminished.

The amount of lubricant in the inlet region is determined by the location of the inlet boundary as shown in Fig. 7. The inlet distance S ahead of the contact region is the distance over which the EHL pressure can build up. By definition,

$$S = x_b - a \quad (1)$$

where x_b is the distance from the lubricant boundary to the center of the Hertzian region and a is the calculated Hertzian radius of dry contact. U_1 and U_2 and the respective surface velocities and h_0 is the resulting film thickness.

This boundary is a function of several variables, including the quantity of lubricant, contact geometry, speed of the bearing surfaces, viscosity, and surface tension. If the lubricant only partially wets the surfaces, this boundary can also be reduced, with an accompanying decrease in film thickness. If the contact is operating with a marginal film thickness, dewetting could drive the contact into the mixed or boundary film regime which would drastically affect the bearing lifetime.

SUMMARY OF RESULTS

1. Thin films of a poly (hexafluoropropene oxide) perfluoropolyether, lot AC (29-2), spontaneously dewetted from the surfaces of 440C stainless steel, 2024 aluminum, and 1018 steel forming droplets which dotted these surfaces.
2. Dewetting did not occur on the surfaces of copper and gold.
3. It was found that dewetting occurred from 440C surfaces at a thickness ≥ 520 Å.
4. Neither a portion of the lot AC (29-2) that was thermally stressed in the presence of oxygen and M-50 steel at 316 °C for 12 days, nor portions that were first filtered through either an alumina or a silica cartridge, dewetted from 440C.
5. A previously non-dewetting lot of HFPO containing varying degrees of perfluorooctanoic acid contamination dewetted from 440C.

CONCLUSIONS

1. Spontaneous dewetting of a particular batch of a poly (HFPO) fluid was caused by the presence of an unknown impurity which is thought to be both thermally labile and polar. The unknown impurity is present at concentrations too low for detection by normal analytical techniques.
2. Care should be taken in selecting batches of poly (HFPO) fluids for critical applications where a dewetting phenomena could lead to premature failure due to lubricant contact starvation.

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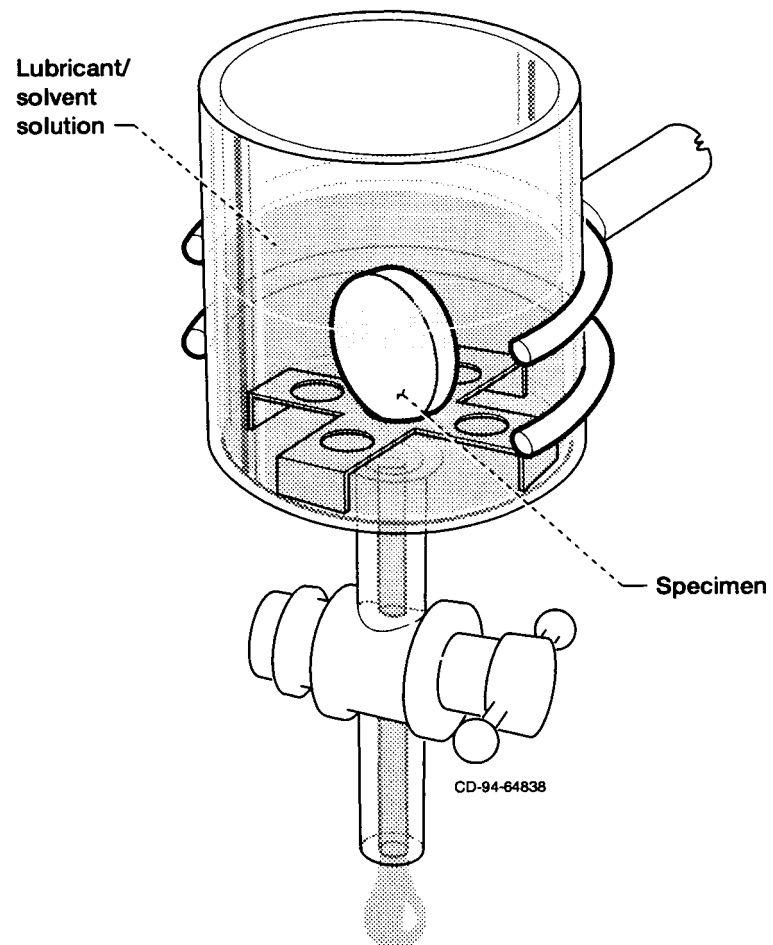


Figure 1.—Film deposition device (FDD).

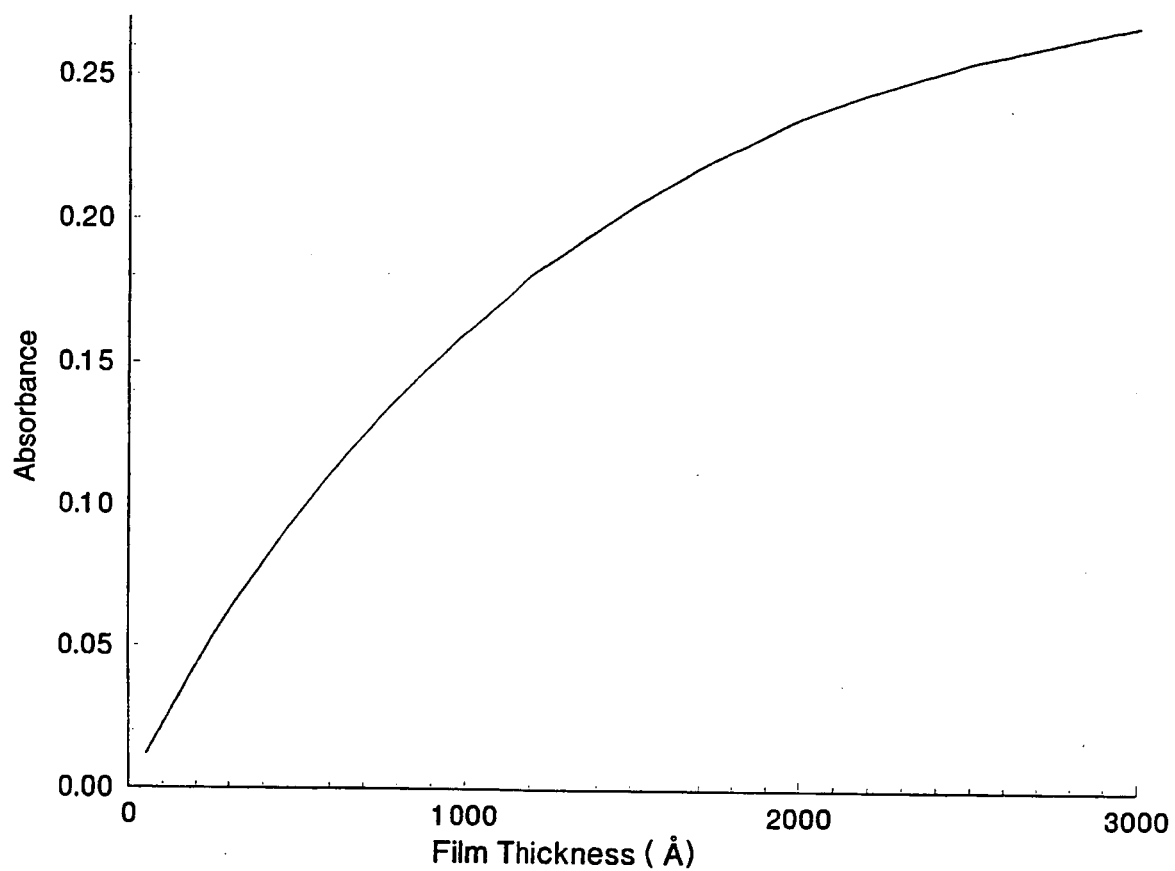


Figure 2. Calculated IR absorbances for the 1313 cm^{-1} band of HFPO as a function of film thickness.

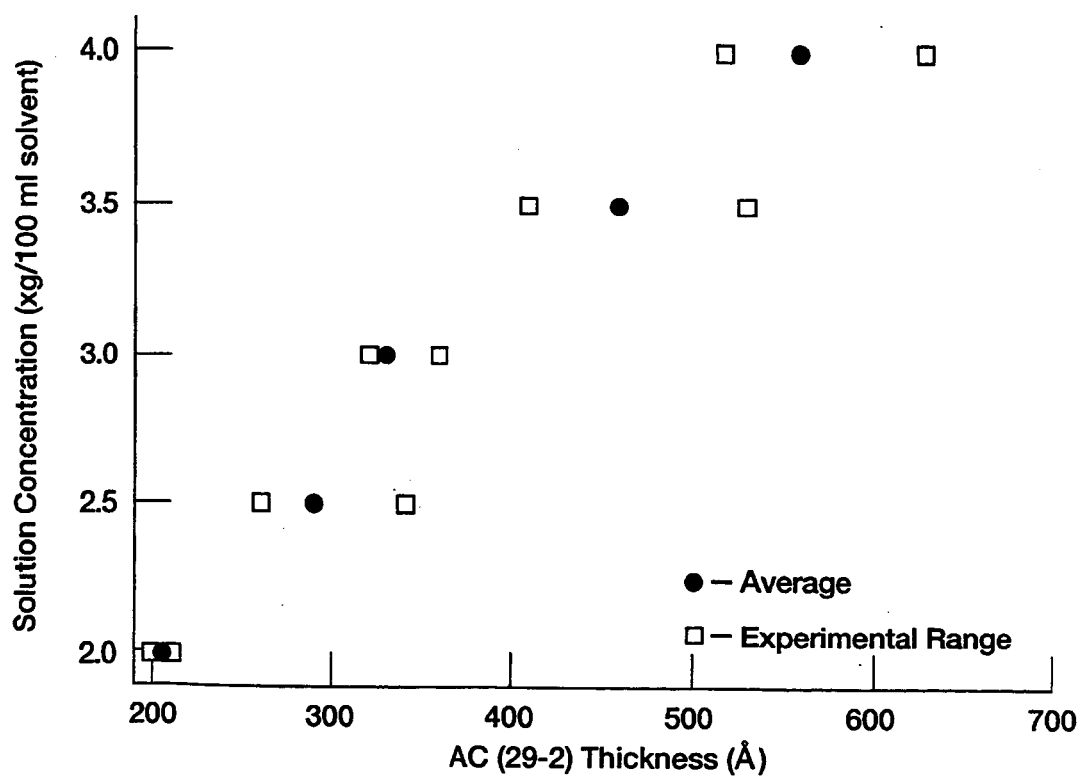


Figure 3. AC (29-2) film thickness as a function of solution concentration.

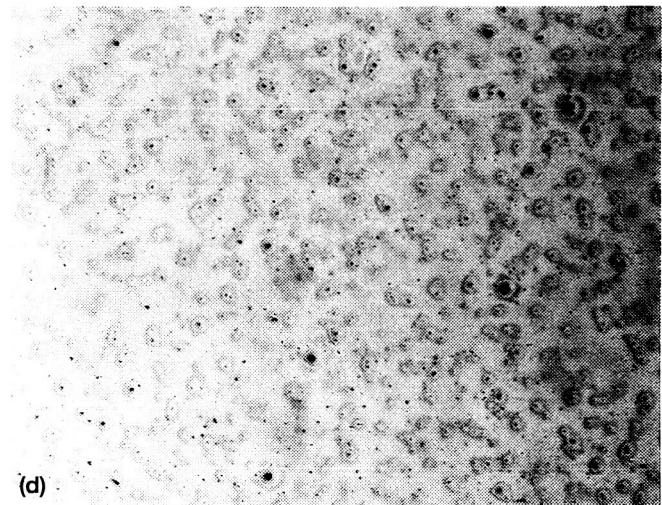
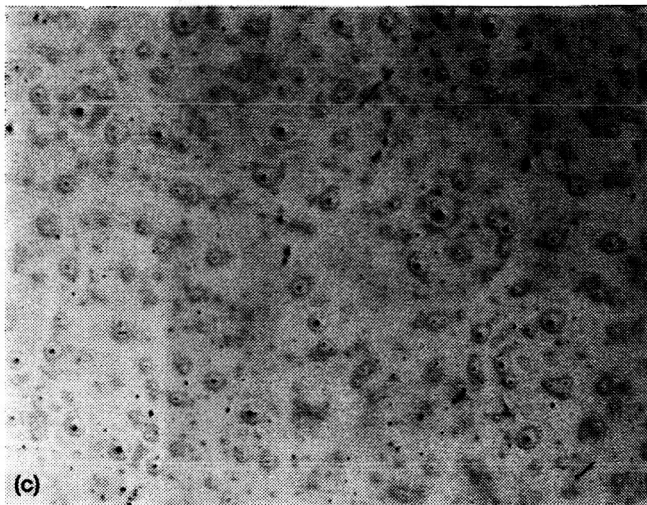
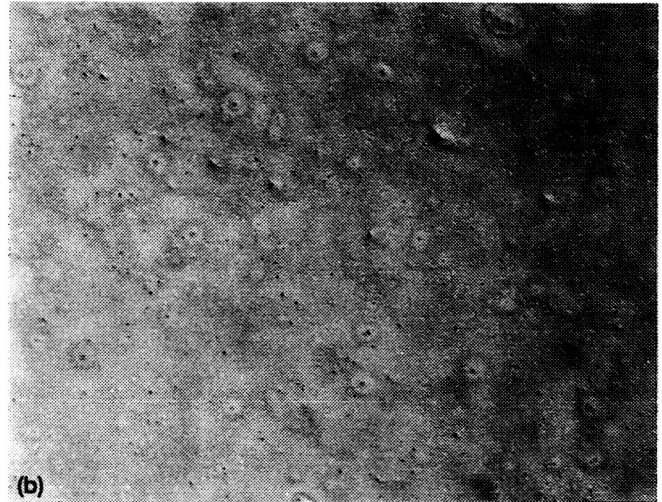
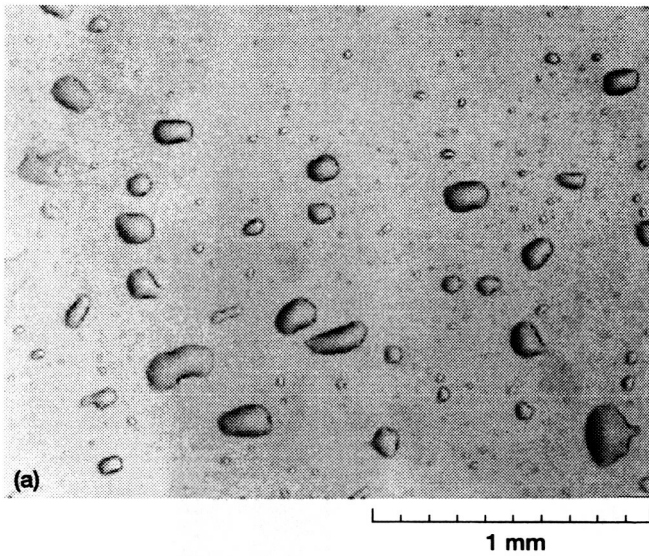


Figure 4.—Micrographs of 440C coated with four different lots of HFPO; (a) Lot AC (29-2), (b) Lot MLO 71-6, (c) Lot 124, (d) Lot 150.

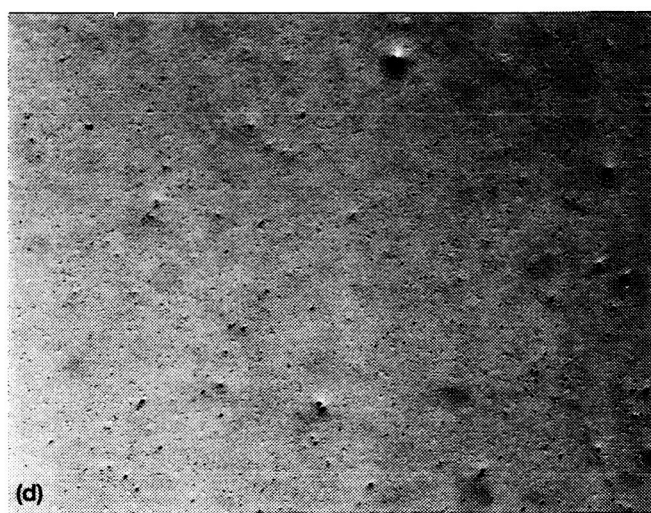
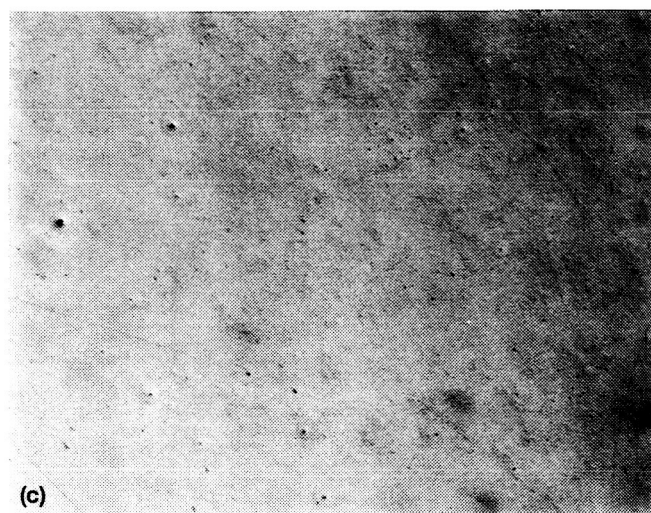
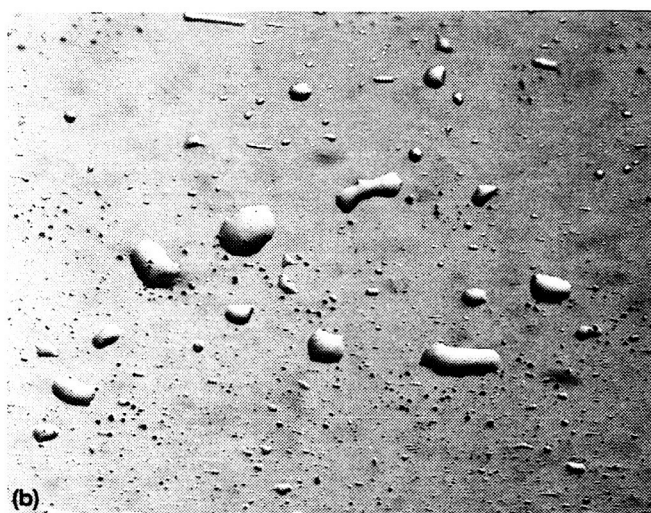
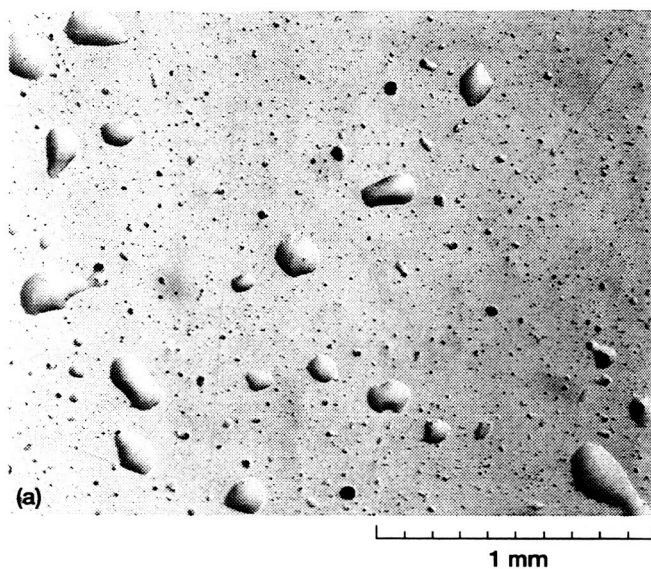


Figure 5.—Micrographs of various metals coated with lot AC (29-2); (a) 2024 aluminum, (b) 1018 steel, (c) Copper, (d) Gold.

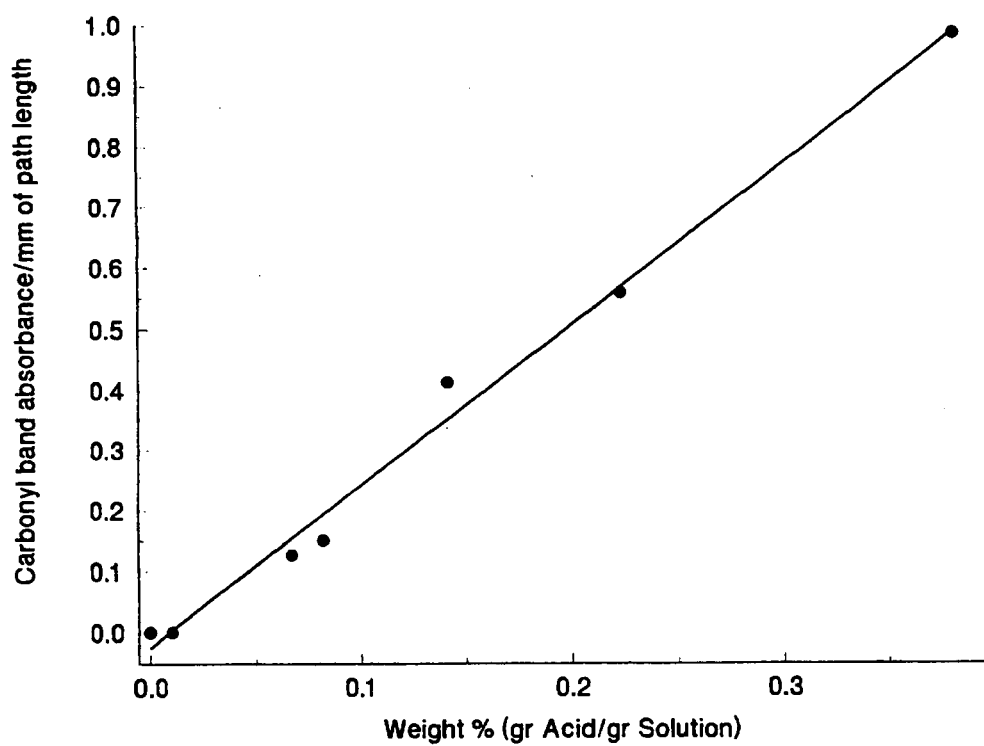


Figure 6. FTIR carbonyl absorbance as a function of acid concentration.

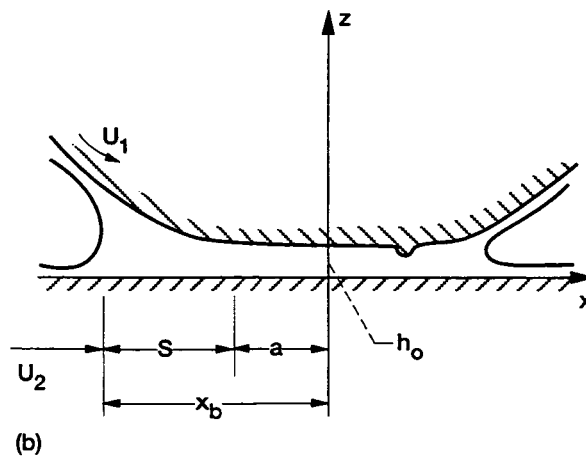
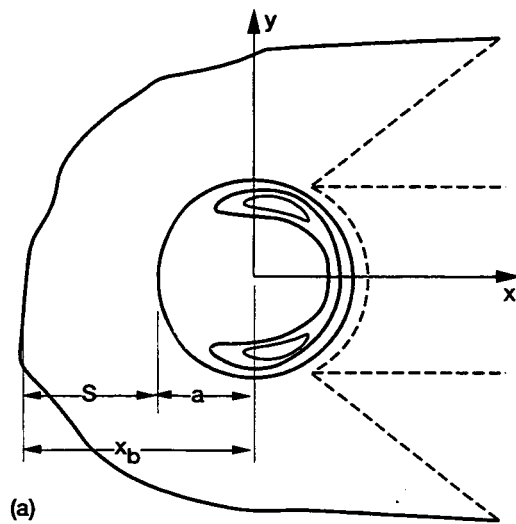


Figure 7.—Ball bearing contact geometry. (a) Plan view.
(b) Cross-sectional view along centerline.

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13. ABSTRACT (Maximum 200 words) Eight different production lots of a commercial perfluoropolyether (PFPE) based on hexafluoropropene oxide (HFPO) were applied to polished metal surfaces by spinning. One of the lots repeatedly dewetted from the clean surface, forming droplets on the surface, whereas the other seven did not dewet. This dewetting phenomenon also repeatedly occurred on 440C steel, 2024 aluminum and 1018 steel, but not on copper or gold. Fourier Transform Infrared Microspectroscopy (μ -FTIR) was used to determine thickness and uniformity of the PFPE films. The dewetting lot was found to dewet from 440C steel at a film thickness greater than 520 Å. A portion of the dewetting lot was heated at 316 °C for 12 days in the presence of oxygen and M-50 steel. This fluid did not dewet. Sequentially, samples of the dewetting lot were filtered either with an alumina or a silica cartridge which can remove polar impurities. Neither of the filtered samples dewetted from 440C steel. It was concluded that an unknown impurity, both thermally labile and polar, present at very low concentration and undetected by our analytical techniques (FTIR, proton NMR, or F^{19} NMR), was responsible for the dewetting phenomenon.				
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